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EP 0467552 A1**EP 0346484 A1****JP 620252496 A****JP 040050288 A****JP 020133666 A**

(58) Field of Search

UK CL (Edition K) C3K KDA, C3V VAG, C4S S670,**G2C CC16****INT CL⁵ C09K****ONLINE DATABASE: WPI**(54) **A microencapsulated photochromic composition for textile printing paste use**

(57) A microencapsulated photochromic composition for textile printing paste use, comprising a microencapsulated solution or dispersion of 1 part by weight of an organic photochromic compound in at least 10 parts by weight of a hindered amine compound e.g. bis-(1, 2, 2, 6, 6-pentamethyl-4-piperidiny) sebacate, 1-[2-[3-(3, 5-di-t-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[3-(3, 5-di-t-butyl-4-hydroxyphenyl)-2, 2, 6, 6-tetramethylpiperidine, or an acrylic oligomer having a weight average molecular weight of 10,000 to 100,000, a textile printing paste containing the above microencapsulated photochromic composition, and a printed article manufactured using the above printing paste. The photochromic compound may be a spiroxazine, spiropyran or pyran compounds, e.g. 6'-substituted spironaphthoxazine.

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A MICROENCAPSULATED PHOTOCHROMIC COMPOSITION FOR
TEXTILE PRINTING PASTE USE

TECHNICAL FIELD

This invention relates to a microencapsulated
5 photochromic composition for textile printing paste use,
a textile printing paste and a printed article.

BACKGROUND ART

There is known the technology of printing a
variety of fabrics with a textile printing paste prepared
10 from an organic compound which has the property to change
color reversibly depending on the presence or absence of
light, which property is known as photochromism (Such an
organic compound is hereinafter referred to briefly as an
organic photochromic compound).

15 For example, there is an oily textile printing
paste prepared by dissolving an organic photochromic
compound directly in a vinyl chloride plastisol or an O/W
aqueous textile printing paste prepared by dissolving an
organic photochromic compound in a solvent and blending
20 the solution with a synthetic resin emulsion.

In the former oily textile printing paste,
which is available on direct dissolution of an organic
photochromic compound, there is inherently a limit to
solubility and the disadvantage that the organic

photochromic compound tends to separate out with time to lower the density of the color which the compound develops on exposure to light. Furthermore, such printed articles are liable to suffer from the migration or transfer of color owing to the influence of a plasticizer which is generally contained in the vinyl chloride plastisol so that they cannot be stored with the colored areas held in contact with each other or in overlap with other materials which are ready to pick up colors.

10 On the other hand, the latter aqueous textile printing paste has the above transfer problem only in a lesser degree but suffers from the same problem as mentioned above that the organic photochromic compound separates out with time.

15 Moreover, organic photochromic compounds in general have an inherent drawback that, irrespective of whether they are used in textile printing pastes or otherwise, they are very sparingly stable against light. To overcome this disadvantage, attempts have been made to
20 dissolve organic photochromic compounds in a variety of high molecular compounds. However, although such attempts may result in improved light fastness, there arises the problem that the sensitivity to light is sacrificed. It is possible to improve the photochromic
25 response by dissolving organic photochromic compounds in

a variety of low molecular high-boiling solvents but this results in compromised light fastness.

Under the circumstances, attempts were made to overcome these disadvantages by incorporating a variety of additives in textile printing pastes containing an organic photochromic compound but there has not been obtained a textile printing paste having the desired photochromic properties, e.g. a satisfactory response to light, and a sufficient light fastness in one.

10 DISCLOSURE OF THE INVENTION

In view of the above state of the art, the present invention was made to provide a photochromic composition having improved printing and photochromic properties and a textile printing paste containing said photochromic composition.

Thus, this invention provides the following microencapsulated photochromic composition, textile printing paste and printed article.

(1) A microencapsulated photochromic composition for textile printing paste use, comprising a microencapsulated solution or dispersion of 1 part by weight of an organic photochromic compound in at least 10 parts by weight of a hindered amine compound or an acrylic oligomer having a weight average molecular weight of 10,000 to 100,000.

(2) A textile printing paste comprising the above microencapsulated photochromic composition and a base printing paste.

(3) A printed article as printed with the above textile printing paste and then subjected to heat treatment or ultraviolet irradiation.

The present inventor found, after much diligent research, that when an organic photochromic compound is dissolved or dispersed in at least 10 times its weight of a hindered amine compound or at least 10 times its weight of an acrylic oligomer with a weight average molecular weight of 10,000 to 100,000, the organic photochromic compound is endowed with improved light fastness and superior photochromic response characteristics. This is presumably because these two kinds of vehicle compounds not only exhibit the function of a polymer to improve light fastness and the function of a low molecular high-boiling solvent to improve photochromic response characteristics but also have a suitable polarity and do not give steric hindrance to the organic photochromic compound. Namely, these two kinds of vehicle compounds provide a field which does not interfere with the change in molecular structure of the organic photochromic compound in its response to light. It was also found that when such a solution or dispersion is

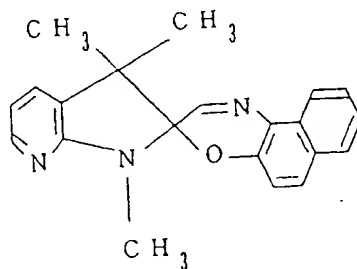
microencapsulated, the favorable field mentioned above is assured to be available at all times and, moreover, the organic photochromic compound is entrapped in microspaces completely secluded from the external environment, with
5 the result that when such a microencapsulated photochromic composition is incorporated in a textile printing paste, the precipitation of the organic photochromic compound with time from the textile printing paste vehicle during storage or on the surface of the printed
10 article is prevented, thus insuring the supply of printed articles completely free of the color migration or transfer problem. It was further discovered that even under the conditions of repeated forward and reverse color reactions in response to intermittent irradiation
15 in the atmospheric air or on long-term persistent exposure to light, the printed article does not experience fatigue, i.e. aging of photochromism, and retains a very satisfactory photochromic response.

This invention will be better understood from
20 the following detailed description, which includes specific examples of various components suitable for the purposes of the invention.

First, as examples of the organic photochromic compound to be employed in this invention, a variety of
25 known spirooxazine compounds, spiropyran compounds and

pyran compounds can be ~~used~~. Thus, among such
 spirooxazine compounds ~~1,3,3~~-trimethylspiro[indoline-
 2,3'-(3H)naphth(2,1-b)(~~1,4~~-oxazine], 5-chloro-1,3,3-
 trimethylspiro[indoline-~~2,3'~~-(3H)naphth(2,1-b)(1,4)-
 5 oxazine] and 1,3,3,5-tetramethylspiro[indoline-2,3'-
 (3H)naphth(2,1-b)(1,4)-~~oxazine~~], which are described in
 the specification of ~~Japan~~ Examined Patent Publication
 No. 28892/1970; 1,3,3-trimethyl-9'-methoxyspiro[indoline-
 2,3'-(3H)naphth(2,1-b)(~~1,4~~-oxazine], 1,3,3,5-tetra-
 10 methyl-9'-methoxyspiro[~~indoline~~-2,3'-(3H)naphth(2,1-b)
 (1,4)-oxazine] and 1,3,3,5-pentamethyl-9'-
 methoxyspiro[indoline-~~2,3'~~-(3H)naphth(2,1-b)(1,4)-
 oxazine, which are ~~described~~ in the specification of
 Japanese Unexamined Patent Publication No. 36284/1980; 4-
 15 trifluoromethyl-1,3,3-trimethyl-5'-methoxyspiro[indoline-
 2,3'-(3H)naphth(2,1-b)(~~1,4~~-oxazine], 6'-trifluoromethyl-
 1,3,3-trimethyl-5'-methoxyspiro[indoline-2,3'-(3H)naphth-
 (2,1-b)(1,4)-oxazine], 4-trifluoromethyl-1,3,3-trimethyl-
 9'-methoxyspiro[indoline-~~2,3'~~-(3H)naphth(2,1-b)(1,4)-
 20 oxazine], which are ~~described~~ in the specification of
 Japanese Unexamined Patent Publication No. 53586/ 1985;
 1,3,5,6-tetramethyl-3-ethylspiro[indoline-2,3'-(3H)pyri-
 do(3,2-f)(1,4)-benzoxazin], 1,3,3,5,6-pentamethyl-
 spiro[indoline-2,3'-(3H)pydo(3,2-f) (1,4)-benzoxa-
 25 zine], 1-methyl-3,3-diphenylspiro[indoline-2,3'-(3H)-

pyrido(3,2-f)(1,4)-benzoxazine], which are described in the specifications of Japanese Unexamined Patent Publications Nos. 112880/1985 and 159458/1986; 1-benzyl-3,3-dimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], 1-(4-methoxybenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], 1-(3,5-dimethylbenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], 1-(4-chlorobenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], 1-(2-fluorobenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], which are described in the specification of Japanese Unexamined Patent Publication No. 233079/1986; 6'-piperidino-1,3,3-trimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], 6'-indolino-1,3,3-trimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], which are described in the specification of Japanese Unexamined Patent Publication No. 33154/1989; and the compound of the following formula:



are 1-(2,3,4,5-pentamethylbenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)-pyran], 1-(2-methoxy-5-nitrobenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)naphth-(2,1-b)-pyran], etc., which are described
5 in the specification of Japanese Unexamined Patent Publication No. 153288/1987.

Among the pyran compounds are 3,3-di-p-methoxyphenyl-3H-naphth(2,1-b)pyran, 2,2-di-p-methoxyphenylphenanthra(2,1-b)pyran, 3,3-diphenyl-3H-naphth(2,1-b)pyran, 2,2-diphenylphenanthra(2,1-b)pyran, etc., which
10 are described in the specification of Japanese Unexamined Patent Publication No. 33154/1989. Aside from the above compounds, spiro[3H-naphth[2,1-b]pyran-3,9'-[9H]-thioxanthene], spiro[3H-naphth[2,1-b]pyran-3,9'-[9H]-xanthene], spiro[2H-naphth[1,2-b]pyran-2,2'-tricyclo-
15 [3,3,1,13,7]decane], 3,3-dimethyl-3H-naphth(2,1-b)pyran, etc. can also be mentioned.

The acrylic oligomer with a weight average molecular weight of 10,000 to 100,000, which is employed
20 in this invention, includes such oligomers as homooligomers or cooligomers of acrylic acid, α -substituted acrylic acid (e.g. methacrylic acid), acrylic acid esters (e.g. methyl acrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, dodecyl
25 acrylate, glycidyl acrylate, etc.), α -substituted acrylic

acid esters (e.g. methyl methacrylate, ethyl methacrylate, butyl methacrylate, octyl methacrylate, glycidyl methacrylate, etc.), acrylamides (e.g. butylacrylamide, hexylacrylamide, etc.), α -substituted
5 acrylamides (e.g. butylmethacrylamide, dibutylmethacrylamide, etc.), acrylonitrile, α -substituted acrylonitrile, hydroxyalkyl acrylate, hydroxyalkyl methacrylate, etc., and cooligomers of the above-mentioned monomers with other vinyl monomers [such
10 as vinyl esters (e.g. vinyl acetate, vinyl butyrate, etc.), vinyl halides (e.g. vinyl chloride), vinyl ethers (e.g. vinyl methyl ether, vinyl octyl ether, etc.), styrene and nuclearly substituted styrene].

The hindered amine compound which can be
15 employed in this invention includes a broad variety of known compounds such as bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (trademark: Sanol LS770, product of Sankyo Co., Ltd.), bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate (tradename: Sanol LS765, product of
20 Sankyo Co., Ltd.), poly[{6-(1,1,3,3-tetramethyl-butyl)amino-1,3,5-triazine-2,4-diyl}{(2,2,6,6-tetramethyl-4-piperidinyl)imino}hexamethylene(2,2,6,6-tetramethyl-4-piperidinyl)imino], 1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine polycondensate, bis-
25 (1,2,2,6,6-pentamethyl-4-piperidyl) 2-(3,5-di-t-butyl-4-

hydroxybenzyl)-2-n-butylmalonate (tradename: Tinuvin 144,
product of Ciba Geigy), 1-[2-{3-(3,5-di-t-butyl-4-
hydroxyphenyl)propionyloxy}ethyl]-4-{3-(3,5-di-t-butyl-4-
hydroxyphenyl)propionyloxy}-2,2,6,6-tetramethylpiperidine
5 (tradename: Sanol LS-2626, product of Sankyo Co., Ltd.),
8'-benzyl-7,7,9,9-tetramethyl-3-octyl-1,3,8-
triazaspiro[4,5]undecane-2,4-dione (tradename: Sanol LS-
1114, product of Sankyo Co., Ltd.), Mark LA57 (product of
Adeka Argus Co., Ltd.), Mark LA 62 (product of Adeka
10 Argus Co., Ltd.), Mark LA67 (product of Adeka Argus Co.,
Ltd.), Mark LA63 (product of Adeka Argus Co., Ltd.), Mark
LA68 (product of Adeka Argus Co., Ltd.), Tinuvin 622 LD
(product of Ciba Geigy) and so on.

In the practice of this invention, the ratio of
15 the acrylic oligomer or hindered amine to the organic
photochromic compound is at least 10 parts by weight and
preferably about 15 to 50 parts by weight relative to
each part by weight of the latter.

Particularly when the spirooxazine compound
20 mentioned above is used as the organic photochromic
compound, it is preferably dissolved or dispersed in the
hindered amine compound. On the other hand when the
pyran compound is used as the organic photochromic
compound, it is preferably dissolved or dispersed in said
25 acrylic oligomer with a weight average molecular weight

of 10,000 to 100,000.

As examples of the particularly preferred combination in this invention, there can be mentioned the combination of a 6'-substituted spironaphthoxazine
5 compound, such as 6'-piperidino-1,3,3-trimethylspiro-[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], with a hindered amine compound in which the amino function is tertiary, such as bis(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate, and the combination of a 3-substituted
10 naphthopyran compound such as 3,3-dimethyl-3H-naphtho(2,1-b)pyran with a methacrylic ester oligomer having a weight average molecular weight of 50,000 to 80,000. In these combinations, the hindered amine compound or the methacrylic ester oligomer assumes an
15 adequate state in terms of hydrophilicity-hydrophobicity balance, reaction stability and viscosity, thus showing very satisfactory workability in the manufacture of microcapsules for printing paste use, and the resulting microencapsulated photochromic composition becomes
20 excellent in light fastness, the density of developed color, photochromic response and other characteristics, thus being quite suited for use in a printing paste.

The microencapsulated photochromic composition of this invention can be manufactured by the following
25 process, for instance.

First, the organic photochromic compound is dissolved in said acrylic oligomer or said hindered amine compound with heating to give an oil. This oil, together with a wall-forming material, is poured in an aqueous or
5 organic solvent containing, where necessary, a surfactant, protective colloid, pH control agent, electrolytes, etc. and emulsified by agitation to form oil droplets. The agitation rate is controlled so that the diameter of the oil droplets will be about 1 to 50 μm , preferably
10 about 3 to 15 μm . In this process, the known microencapsulation technique such as interfacial polymerization, in situ polymerization, coacervation, etc. can be utilized to give the microencapsulated photochromic composition.

15 The wall-forming material mentioned above for covering said oil droplets includes such high molecular compounds as polyurea, polyamide, polyester, polyurethane, epoxy resin, urea resin, melamine resin, gelatin, ethylcellulose, polystyrene, polyvinyl acetate and so on.
20 In this microencapsulation process, such wall-forming material can be used in the routine amount which may be selected from a broad range. For example, the wall-forming material may be used in a proportion of about 0.1 to 1 part by weight per part by weight of the core
25 organic photochromic compound plus the hindered amine

compound or the acrylic oligomer.

The surfactant, protective colloid, pH control agent, electrolytes and organic solvent mentioned above may be those which are commonly used in microencapsulation processes.

The surface of the photochromic particles or granules in the resulting composition can be subjected to crosslinking reaction with, for example, melamine resin, urea resin, epoxy resin, an aldehyde compound or an isocyanate compound. Crosslinking hardens the capsule wall and improves its heat resistance.

The preferred microencapsulated photochromic composition is one in which the surface of the thermosetting capsule wall has been coated with a hydrophilic high molecular compound such as gum arabic, gelatin, polyvinylpyrrolidone, polyvinyl alcohol, carboxymethylcellulose, methylcellulose, ethylcellulose, sodium polyacrylate, polyacrylamide, styrene-maleic anhydride copolymer, ethylene-maleic anhydride copolymer and so on. This coating can be carried out by the known technique such as in situ coating, coacervation, air suspension coating, interfacial precipitation and so on. The resulting microencapsulated photochromic composition features a non-thermoplastic and seamless wall structure.

In the microencapsulated photochromic

composition of this invention, the organic photochromic compound exists in microspaces which are completely secluded from the external environment. Therefore, not only the transfer or migration of color is prevented but
5 the precipitation due to crystallization is precluded at the same time. As a result, the degree of freedom in regard of storage conditions is increased and the aging of color density can be completely prevented.

Moreover, as the organic photochromic compound
10 is allowed to be present at all times in a large excess of the acrylic oligomer or hindered amine vehicle, there are realized outstanding light fastness and excellent photochromic characteristics with high efficiency which could never be implemented by the prior art.

15 The microencapsulated photochromic composition of this invention may contain not only said organic photochromic compound and either said acrylic oligomer or said hindered amine compound but various additives which have heretofore been used in this technical field, such
20 as plasticizers, solvents, antioxidants, infrared absorbers, singlet oxygen light quenchers, dyes, pigments, oils and waxes wherever necessary. The proportion of such additives is preferably up to about 30% by weight based on the total amount of said organic
25 photochromic compound and said acrylic oligomer or

hindered amine compound. With the additives within this range, the density of color can be increased or the hue be modified as desired.

A photochromic compound-containing textile printing paste can be obtained by adding the microencapsulated photochromic composition of this invention to a base printing paste. The base printing paste in which the microencapsulated photochromic composition is incorporated may be any of the conventional aqueous and oily textile printing pastes. As specific examples of such textile printing pastes, there can be mentioned aqueous pastes comprising synthetic resin emulsions or water-soluble polymers and oily pastes comprising vinyl chloride plastisols, ultraviolet curable resin pastes or the like.

The synthetic resin emulsions for said aqueous pastes may be any known synthetic resin emulsions for textile printing use, such as emulsion copolymers or emulsion polymers in the acrylic acid ester, butadiene, acrylonitrile-styrene, vinyl chloride, vinylidene chloride or vinyl acetate series. Moreover, for improved bonding to fiber, an emulsion using a thermosetting acrylic ester copolymer alone or an emulsion using an acrylic ester copolymer and a thermosetting resin, e.g. melamine resin, urea resin or the like, in combination

can be utilized. In using these emulsions, the known curing catalysts, such as a hydrochloride of an organic amine, various metal salts thereof, etc. can be incorporated.

5 The water-soluble high molecular compounds may be those hydrophilic high molecular compounds which can be used for the formation of the microcapsul wall.

 The aqueous paste may comprise said synthetic resin emulsion or said water-soluble high molecular
10 compound or both.

 The vinyl chloride plastisol mentioned above may be any of the vinyl chloride plastisols in common use. For example, there can be employed a synthetic resin paste comprising a resin component such as vinyl
15 chloride resin, vinyl chloride copolymer, etc., a plasticizer such as dioctyl phthalate (DOP), dioctyl adipate (DOA), dioctyl sebacate (DOS), chlorinated paraffin, etc., a stabilizer such as tribasic lead, dibasic lead phosphite, dibasic lead phthalate, lead
20 stearate, cadmium stearate, dibutyltin laurate, etc., a lubricant such as a fatty acid (e.g. stearic acid, palmitic acid, etc.), an ester thereof, an ether thereof, a wax, etc., and a filler such as barium sulfate, calcium carbonate and so on.

25 The ultraviolet-curable resin paste may be any

of the known UV-curable resin pastes, such as one comprising a photosensitive prepolymer in the unsaturated polyester, epoxy acrylate, urethane acrylate or other series, a binder polymer component such as povals, polyamides, polymethacrylates, etc., a monomer component such as acrylates, methacrylates, etc., and a photopolymerization initiator in the benzoin, acetophenone, benzil ketal, aminoketone or the like series.

In the above aqueous textile printing paste or oily textile printing paste, the microencapsulated photochromic composition of this invention can be incorporated with great freedom, namely in any proportion. However, the preferred proportion is generally about 1 to 50 parts by weight based on 100 parts by weight of such a paste.

If desired, the textile printing paste may contain a variety of additives which are commonly used in textile printing pastes, such as thickeners, thermosetting resins, curing catalysts, surfactants, discharge agents, anti-dyeing agents, dyes, pigments, fluorescent pigments, fluorescent dyes, extender pigments, thermochromic substances, light storage pigments, light-emitting pigments of UV excitation type, metal powders, preservatives, antifoams, foaming agents, dryness modulating agents, antistatic agents, ultraviolet

absorbers, ultraviolet stabilizers, antioxidants, perfumes and so on.

The textile printing paste of this invention, which can be obtained as above, can be printed on a
5 portion or the entire surface of a substrate fabric by any of the known printing techniques such as roll printing, rotary printing, screen printing, spray printing and so on.

The fabric which can be printed with the
10 textile printing paste according to this invention includes, inter alia, the woven fabrics, knit fabrics, blended fabrics, mix-woven fabrics, etc. of natural fibers, such as cotton, linen, silk, wool, etc., regenerated or semi-synthetic fibers, such as rayon,
15 cuprammonium, polynosics, acetate and other fibers, or synthetic fibers in the polyolefin, polyamide, polyester, polyacrylic, polyvinyl and other series. There may also be mentioned synthetic leathers and synthetic resin films and sheets in the vinyl chloride, polyurethane, polyamide
20 and other series.

After printing with the textile printing paste of this invention, the printed fabric is subjected to preliminary drying and, then, to heat treatment or ultraviolet curing treatment, whereupon the
25 microencapsulated photochromic composition is bound to

the fiber by the adhesive action of the synthetic resin emulsion, water-soluble high molecular compound, vinyl chloride plastisol or ultraviolet-curable resin to give a finished printed article.

5 The heat treatment can be carried out generally at about 90 to 200°C for about 10 seconds to 5 minutes. The ultraviolet curing treatment is carried out when a UV-curable resin paste is employed. The conditions of this treatment may be the same as those used in the
10 conventional UV irradiation procedure and can be selected according to the kind of ultraviolet curable resin incorporated and the printing thickness thereof. As an example, the printed fabric is irradiated with a mercury vapor lamp of about 80 W/cm-160 W/cm rating at an
15 irradiation distance of not greater than 15 cm for a time period of not greater than 10 seconds.

 After the above heat treatment or ultraviolet curing treatment, the printed fabric is subjected to soaping, rinse, resin processing, etc. in the con-
20 ventional manner.

 When a textile printing paste containing the microencapsulated photochromic composition of this invention is employed, printed articles having excellent light fastness, color density, chromic sensitivity, color
25 reversal time, heat resistance, rubbing resistance and

other characteristics, as well as a broad range of color variation and a variety of hues, can be obtained for a diversity of applications.

Examples

5 The following examples are intended to further clarify the features of this invention.

Example 1

While 100 parts by weight (hereinafter referred to briefly as parts) of a 15% aqueous solution of gelatin
10 was heated under reflux at 85°C, a molten mixture of 4 parts of 6'-indolino-1,3,3-trimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], 60 parts of bis-(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate, 10 parts of epoxy resin ("Epikote 828", product of Yuka Shell
15 Epoxy Co., Ltd.) and 6 parts of a curing agent for epoxy resin ("Epicure Z", Yuka Shell Epoxy Co., Ltd.) was added with constant stirring and while the agitation speed was controlled to insure formation of oil droplets with an average diameter of 10 μ m, the reaction was continued for
20 1 hour to give cured oil droplets. The system was then cooled and filtered and the resulting granules were rinsed and dried to give about 80 parts of a microencapsulated photochromic composition.

Then, 20 parts of this composition was mixed
25 with 75 parts of an acrylic ester resin emulsion (binder

for textile printing use, "Binder 350R", product of Matsui Shikiso Chemical Co., Ltd.) and 5 parts of an epoxy-type crosslinking agent to give a textile printing paste.

5 Using a 1 cm (dia.) polka dot-patterned screen (80 mesh), the above paste was printed on a cotton broad-cloth and subjected to drying and, then, to heat treatment at 140°C for 3 minutes.

 This printed cloth was a solid white cloth in a
10 room not exposed to direct sunlight but became a blue polka-dotted cloth at the sunlit window and outdoors. When the cloth was brought back into the room, it returned to a solid white cloth, thus exhibiting a reversible and satisfactory photochromic response. The
15 light fastness of this printed cloth corresponded to Grade 6-7 (JIS L0842 and JIS L0843; the same applies hereafter).

 The same printed cloth was re-examined after 3,
10 and 30 days. As a result, there was no
20 crystallization of the organic photochromic compound, nor was the consequent decrease in the density of color. (Table 1).

Example 2

 A microencapsulated photochromic composition
25 was prepared in the same manner as Example 1 except that

60 parts of bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate was used in lieu of 60 parts of bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate. Using this microencapsulated photochromic composition, a textile printing paste was prepared and printed on a cotton broadcloth as in Example 1 to give a printed cloth. For each of the above printing paste and printed cloth, the light fastness, degree of crystallization of the organic photochromic compound and the density of developed color were determined. The results are shown in Table 1.

Comparative Example 1

A microencapsulated photochromic composition was prepared in the same manner as Example 1 except that 1 part of bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate and 59 parts of xylene were used in lieu of 60 parts of bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate. Using this microencapsulated photochromic composition, a textile printing paste was prepared and printed on a cotton broadcloth as in Example 1 to give a printed cloth. For each of the above printing paste and printed cloth, the light fastness, the degree of crystallization of the organic photochromic compound and the density of developed color were determined. The results are shown in Table 1.

Comparative Example 2

A printed cloth was manufactured in the same manner as Comparative Example 1 except that 4 parts of bis(1,2,2,6,6-pentamethyl-4-piperidiny1) sebacate and 56 parts of xylene were used. For each of the printing paste and printed cloth, the light fastness, the degree of crystallization of the organic photochromic compound and the density of developed color were determined. The results are shown in Table 1.

Comparative Example 3

A printed cloth was manufactured in the same manner as Comparative Example 1 except that 8 parts of bis(1,2,2,6,6-pentamethyl-4-piperidiny1) sebacate and 52 parts of xylene were used. For each of the printing paste and printed cloth, the light fastness, the degree of crystallization of the organic photochromic compound and the density of developed color were determined. The results are shown in Table 1.

Comparative Example 4

One part of 6'-indolino-1,3,3-trimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine] and 15 parts of bis(1,2,2,6,6-pentamethyl-4-piperidiny1) sebacate were dissolved under heating and the resulting solution was admixed with 75 parts of an acrylic ester resin emulsion ("Binder 350R") and 5 parts of an epoxy-type crosslinking agent under stirring to

give a printing paste.

Using a 1 cm (dia.) polka-dotted screen (80 mesh), the above printing paste was printed on a cotton broadcloth and heat-treated at 140°C for 3 minutes.

5 For each of the above printing paste and printed cloth, the light fastness, the degree of crystallization of the organic photochromic compound and the density of developed color were determined. The results are shown in Table 1.

10 Comparative Example 5

One part of 6'-indolino-1,3,3-trimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxadine], 1 part of bis(1,2,2,6,6-pentamethyl-4-piperidiny) sebacate and 14 parts of xylene were
15 dissolved under heating and the solution was admixed with 75 parts of an acrylic ester resin emulsion ("Binder 350R") and 5 parts of an epoxy-type crosslinking agent under stirring to give a printing paste.

Using a 1 cm (dia.) polka-dotted screen (80
20 mesh), the above printing paste was printed on a cotton broadcloth and subjected to heat treatment at 140°C for 3 minutes.

For each of the above printing paste and printed cloth, the light fastness, the degree of
25 crystallization of the organic photochromic compounds and

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the density of developed color were determined. The results are shown in Table 1.

Table 1

	Light fastness	Aging resistance of printing paste	Aging resistance of printed cloth	Density of color after one month of repeated exposure to light with a frequency of 5 times a day
Example 1	Grade 6-7	No precipitation of organic photochromic compound crystals even after 1 month	No precipitation of organic photochromic compound crystals even after 1 month	100%
Example 2	Grade 4	Same as above	Same as above	70%
Comparative Example 1	Grade 1	Same as above	Same as above	10%
Comparative Example 2	Grade 1-2	Same as above	Same as above	15%
Comparative Example 3	Grade 2	Same as above	Same as above	20%
Comparative Example 4	Grade 3	Precipitation of organic photochromic compound crystals and a decrease in density of developed color were found after 1 day.	Precipitation of organic photochromic compound crystals and a decrease in density of developed color were found after 3 days.	10%
Comparative Example 5	Grade 1	Same as above	Same as above	5%

Example 3

Thirty parts of 3,3-diphenyl-3H-naphtho[2,1-b]pyran,
400 parts of an oligomer (weight average molecular weight
65000) prepared by copolymerising a methyl methacrylate
5 and butyl methacrylate (1:1), 100 parts of toluene, 20
parts of an antioxidant ("Sumilizer BHT", product of
Sumitomo Chemical Co., Ltd.) and 80 parts of an epoxy
resin ("Epikote 828") were melted together under heating
and the mixture was poured in 1,000 parts of a 5% aqueous
10 solution of hydroxyethylcellulose previously heated to
80°C under constant stirring. The stirring speed was
controlled so that the average particle size of the
dispersion was about 8 µm. Then, 30 parts of a curing
agent for epoxy resin ("Epicure U", product of Yuka Shell
15 Epoxy Co., Ltd.) was added and the mixture was further
stirred, with the liquid temperature being gradually
increased to 95°C. The reaction was continued for 2
hours to give a dispersion containing about 650 parts of
photochromic microcapsules. Then, 20 parts of the above
20 dispersion was mixed with 75 parts of an oil-in-water
emulsion comprising a butadiene-styrene emulsion
copolymer (solid content of 40%), terpene and an acrylic
ester copolymer emulsion (solid content of 38%) to give a
textile printing paste containing photochromic
25 microcapsules. This printing paste was printed on a

blue-colored cotton broadcloth using a fruit-patterned screen (120 mesh). This cloth was a solid blue cloth in a room not exposed to direct sunlight but at the sunlit window or outdoors a brilliant green fruit pattern appeared on the cloth. When the cloth was brought back into the room, it became a solid blue cloth again, indicating a very satisfactory and reversible photochromic response. The light fastness of this printed cloth was Grade 6-7.

10 While this printed cloth was re-examined after 3, 10 and 30 days, there was found no crystallization of the organic photochromic compound, nor was found a decrease in the density of color.

Example 4

15 To a mixture of 10 parts of 6'-piperidino-1,3,3-trimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine] and 240 parts of Mark LA52 (product of Adeka Argus Co., Ltd.) was added 50 parts of a polyvalent isocyanate ("Millionate MR", product of Nippon
20 Polyurethane Industry Co., Ltd.) followed by heating with stirring to give a homogeneous solution. Then, this solution was added to 2,000 parts of an aqueous solution containing 10 parts of colloidal tricalcium phosphate and 0.2 part of sodium dodecylbenzenesulfonate as dispersion
25 stabilizers and pre-warmed to 60°C. The mixture was

stirred at an agitation speed controlled so that the average particle size of the dispersion in water was 5 μm . Then, 10 parts of xylylenediamine was added dropwise to the above dispersion and the stirring was further continued at 60°C for about 3 hours to complete the reaction. The reaction mixture was then filtered, rinsed and dried to give about 310 parts of a microencapsulated photochromic composition. One-hundred parts of this microencapsulated photochromic composition was added to 500 parts of a 10% aqueous solution of gelatin at 40°C and the mixture was stirred well. This dispersion was then added to 1,000 parts of 3% gum arabic solution under constant stirring and after pH adjustment to 4.5 with 10% acetic acid, about 500 parts of water was further added for coacervation. Then, 70 parts of 20% formalin was added and the mixture was gradually cooled to a liquid temperature of 5°C or below. The system was stirred at a temperature not exceeding 5°C for 30 minutes, after which it was adjusted to pH 9.5 with a 10% aqueous solution of sodium hydroxide. Thereafter, the liquid temperature was increased at the rate of 1°C/minute to 50°C, whereby a dispersion of polyurea-gelatin double-walled microcapsules having an average grain size of 10 μm was obtained. The dispersion was rinsed and filtered and the resulting granules were allowed to dry to give about 150

parts of a microencapsulated photochromic composition.

Then, using a floral-patterned screen (80 mesh), a textile printing ink prepared from 20 parts of the above microencapsulated photochromic composition and 80 parts of an acrylic ester-type resin emulsion ("Binder 350R") was printed on synthetic leather of nylon in a dry thickness of about 30 μm , dried and heat-treated at 140°C for 5 minutes.

This synthetic leather was cut and machine-sewed to fabricate children's sandals. These sandals had the intrinsic color of synthetic leather in the room not exposed to direct sunlight but a purple-colored floral pattern appeared at the sunlit window or outdoors. When these sandals were brought back into the room, the original color resumed. The forward and reverse color reactions could be repeated a number of times. The light fastness of the pattern corresponded to Grade 7. Even after 1 month, there was no precipitation of the organic photochromic compound, nor was found a fatigue of color.

20

Example 5

A homogeneous hot solution composed of 10 parts of 6'-indolino-1,3,3-trimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine], 160 parts of 1-[2-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-

25

tetramethylpiperidine and 25 parts of epoxy resin ("Epikote 815", product of Yuka Shell Epoxy Co., Ltd.) was poured in 500 parts of a 10% aqueous solution of gelatin at 60°C and the agitation speed was controlled to
5 obtain a dispersion of oil droplets with a diameter of about 10 μ m. Then, 10 parts of a curing agent for epoxy resin ("Epicure U") was added and the agitation was continued at an elevated temperature of 95°C for 2 hours. The system was cooled and the product microcapsules were
10 collected by filtration, rinsed and dried to give about 200 parts of a microencapsulated photochromic composition.

One-hundred parts of the above microencapsulated photochromic composition was added to 500 parts of a 1%
15 aqueous solution of carboxymethylcellulose at 60°C with constant stirring to give a homogeneous suspension. Then, under further stirring, 30 parts of a 30% aqueous solution of a melamin-formaldehyde prepolymer was added and the liquid temperature was increased to 95°C. There-
20 after, the system was adjusted to pH 5.5 with 10% acetic acid and further stirred for 2 hours. The system was then cooled and the microcapsules formed were recovered by filtration, rinsed and dried to give about 110 parts of a microencapsulated photochromic composition in which
25 the organic photochromic compounds had been entrapped in

the non-thermoplastic resin covered with crosslinked melamin-formaldehyde resin.

Ten parts of the above microencapsulated photochromic composition was formulated with 0.1 part of a red
5 organic pigment ("Novaperm Red HF-3F", product of Hoechst Co., Ltd.), 2 parts of titanium dioxide (TiO_2 JR 701", product of Teikoku Kako Co., Ltd.), 45 parts of vinyl chloride resin ("Geon 121", product of Nippon Zeon Co., Ltd.), 30 parts of DOP, 15 parts of a polyester-type
10 plasticizer, 1 part of dibutyltin laurate and 1 part of a nonionic surfactant ("Solgen 30", product of Dai-Ichi Kogyo Seiyaku Co., Ltd.) and the resulting vinyl chloride plastisol was printed on a cotton T-shirt using a floral-patterned screen (80 mesh) in a dry thickness of about 50
15 μm and subjected to heat treatment at 180°C for 3 minutes.

The floral pattern of the T-shirt was red in the room not exposed to direct sunlight but assumed a brilliant purple color at the sunlit window or outdoors.
20 When the shirt was brought back into the room, the pattern on the T-shirt became red again. This reversible phenomenon could be repeated a number of times. The light fastness corresponded to Grade 7 and there was no migration of color.

Example 6

A vinyl chloride plastisol was prepared in the same manner as Example 5 except that 10 parts of Chromicolor Fast Yellow #27 (trademark: a thermochromic material manufactured by Matsui Shikiso Chemical Co., Ltd.) was used in lieu of 0.1 part of the red organic pigment. A cotton T-shirt printed to a floral pattern was then manufactured in the same manner as Example 5. The floral pattern thus printed was yellow in the room not exposed to direct sunlight at 20°C but outdoors it assumed a brilliant green color. When the temperature was increased to 35°C in this state, the floral pattern became blue. Then, with this temperature of 35°C being maintained, the T-shirt was brought back into the room not exposed to sunlight, whereupon the floral pattern on the T-shirt faded away. When the temperature was decreased back to 20°C, the initial yellow floral pattern reappeared. This reversible thermal-optical chromic reaction could be repeated a number of times. The light fastness and the degree of color migration were comparable to those of the fabric manufactured in Example 5.

Example 7

A vinyl chloride plastisol was prepared in the same manner as Example 5 except that the red organic pigment

was not employed.

Using a floral-patterned screen (80 mesh), the above vinyl chloride plastisol was printed on a polyester cloth in a dry thickness of about 50 μ m and subjected to heat treatment at 180°C for 3 minutes.

This cloth had a solid white color in the room not exposed to direct sunlight but showed a brilliant blue floral pattern at the sunlit window and outdoors. The light fastness corresponded to Grade 7 and no migration of color took place.

For each of the above printing paste and printed cloth, the light fastness, the degree of crystallization of the organic photochromic compound, the density of color developed, and the degree of color migration were determined. The results are shown in Table 2.

Comparative Example 6

A vinyl chloride plastisol was prepared in the same manner as Example 5 except that, in lieu of said microencapsulated photochromic composition and red organic pigment, 0.5 part of 6'-indolino-1,3,3-trimethylspiro[indoline-2,3'-(3H)naphth(2,1-b)(1,4)-oxazine] and 8 parts of 1-[2-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]ethyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-tetramethylpiperidine were used.

Using the above vinyl chloride plastisol, a floral printed polyester cloth was prepared as in Example 7.

For each of the above printing paste and printed cloth, the light fastness, the degree of crystallization
5 of the organic photochromic compounds, the density of developed color and the degree of color migration were determined. The results are shown in Table 2.

Table 2

	Light fastness	Aging resistance of printing paste	Aging resistance of printed cloth	Density of color after one month of repeated exposure to light with a frequency of 5 times a day	Migration of color
Example 7	Grade 7	No precipitation of organic photo-chromic compound crystals even after 1 month	No precipitation of organic photo-chromic compound crystals even after 1 month	100%	No migration of color was observed after 1-month storage with printed areas overlapped at room temperature for 1 month.
Comparative Example 6	Grade 3	Precipitation of organic photo-chromic compound crystals and a decrease in density of developed color were found after 1 day.	Precipitation of organic photo-chromic compound crystals and a decrease in density of developed color were found after 3 days.	10%	A marked migration of color occurred, with the floral pattern smeared out, after 1-day storage with printed areas overlapped.

CLAIMS:

1. A microencapsulated photochromic composition for textile printing paste use, comprising a microencapsulated solution or dispersion of 1 part by weight of an organic photochromic compound in at least 10 parts by weight of a hindered amine compound or an acrylic oligomer having a weight average molecular weight of 10,000 to 100,000.
2. The microencapsulated photochromic composition of claim 1 wherein said organic photochromic compound is a spirooxazine compound as dissolved or dispersed in said hindered amine compound.
3. The microencapsulated photochromic composition of claim 1 wherein said organic photochromic compound is a pyran compound as dissolved or dispersed in said acrylic oligomer.
4. The microencapsulated photochromic composition of claim 2 wherein said organic photochromic compound is a 6'-substituted spironaphthoxazine and the amino function of said hindered amine compound is a tertiary one.
5. The microencapsulated photochromic composition of claim 3 wherein said organic photochromic compound is a 3-substituted naphthopyran compound and said acrylic oligomer is a methacrylic ester oligomer having a weight average molecular weight of 50,000 to 80,000.

6. A photochromic textile printing paste comprising the microencapsulated photochromic composition of claim 1 and a base printing paste.

7. The printing paste of claim 6 wherein said base
5 printing paste is an aqueous paste comprising a synthetic resin emulsion and/or a water-soluble high molecular compound or an oily paste comprising a vinyl chloride plastisol or a ultraviolet light-curable resin paste.

8. A printed article obtainable by printing with the
10 textile printing paste of claim 6 and subsequent heat treatment or ultraviolet light treatment.

Patents Act 1977
 Examiner's report to the Comptroller under
 Section 17 (The Search Report)

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Application number

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Relevant Technical fields

(i) UK CI (Edition L) C4S (SG70), C3K (KOA); C3V
 (VAG); G2C (CC16)

(ii) Int CI (Edition 5) C09K

Search Examiner

MS N R CURTIS

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: WPI

Date of Search

24.11.92

Documents considered relevant following a search in respect of claims 1-8

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
A	EP 0467552 A1 (LINTEC) page 2, lines 51-54; page 11; lines 36-44	1,4
A	EP 0346484 A1 (JAPAN CAPSULAR PRODUCTS) see Claim 6	1,2
Y	JP 62052496 (NIPPON SHEET GLASS) Derwent WPI Acc. No. 87/350903/50	Claim 1 at least
X Y	JP 040050288 (MATSUI CHEM. IND.) Derwent WPI Acc. No. 92/109250/14	Claims 1, 2 at least 1 at least
Y	JP 020133666 (TORAY IND. INC.) Derwent WPI Acc. No. 90-204176127	Claim 1 at least

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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